CHAPTER 2

EPA/NSF ETV
EQUIPMENT VERIFICATION TESTING PLAN FOR OZONE AND ADVANCED OXIDATION PROCESSES FOR INACTIVATION OF MICROBIOLOGICAL CONTAMINANTS

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1.0 APPLICATION OF THIS VERIFICATION TESTING PLAN

This document is the Environmental Technology Verification (ETV) Plan for evaluation of water treatment equipment utilizing ozone and advanced oxidation for inactivation of microorganisms. This Testing Plan is to be used as a guide in the development of the Product-Specific Test Plan (PSTP) for testing ozone and advanced oxidation equipment, within the structure provided by the "EPA/NSF ETV Protocol For Equipment Verification Testing For Inactivation Of Microbiological Contaminants: Requirements For All Studies." This ETV plan is applicable only to water treatment systems that rely on ozone and advanced oxidation to inactivate microorganisms. Water treatment systems using ozone oxidation for reasons other than disinfection (i.e. taste and odor control, inorganics oxidation) are not required to conduct the experiments outlined in this ETV plan, as long as adequate disinfection is being achieved by other technologies (e.g., chlorine or chloramines). Ozone is sometimes combined with ultraviolet (UV) light or hydrogen peroxide to improve oxidation. These advanced oxidation processes (AOPs) can also be tested under this plan.

In order to participate in the equipment verification process for microbial inactivation by ozone and advanced oxidation, the equipment Manufacturer and their designated Field Testing Organization shall use the procedures and methods described in this test plan, and in the "Protocol for Equipment Verification Testing for Inactivation of Microbiological Contaminants: Requirements for All Studies" as guidelines for development of the PSTP.

This ETV test plan is applicable to the testing of water treatment equipment utilizing ozone and advanced oxidation for inactivation of microorganisms in drinking water. This plan is applicable to both surface water and ground water supplies.

2.0 INTRODUCTION

Ozone is a powerful oxidant that is applied during water treatment for microbial inactivation as well as oxidation of pesticides, metals, and taste and odor causing compounds. The use of ozone in potable water treatment in the United States has increased substantially in the last 20 years, due to its superior inactivation of microorganisms (e.g., cysts) relative to chlorine, chloramine, and chlorine dioxide.

Ozone is applied to drinking water as a gas, which is generated on-site. The ozone gas is transferred into a dissolved state by either bubbling or injecting ozone gas into the process stream. Ozone can be applied to untreated (raw) or treated (e.g., coagulated/settled or filtered) water.

In this ETV test plan, ozone or AOP equipment performance can be verified in one of two ways: 1) by achieving a certain level of "CT" [concentration, *C* (in mg/L), of ozone multiplied by contact time, *T* (in minutes)] during treatment; or 2) by conducting microbial seeding or challenge testing by measuring the microbial inactivation (for a variety of microorganisms) achieved by the ozone or by AOPs.

Ozone CT values have been established by the USEPA for virus and *Giardia* cyst inactivation for use in guiding state regulatory agencies in the implementation of the filtration and disinfection rules. While the USEPA has not yet established CT requirements for *Cryptosporidium* inactivation, CT values can be determined in this ETV plan to establish the level of CT that can be achieved with the ozone or some types of AOP equipment. Thus, many ozone systems will be able to use the CT approach in this ETV plan.

AOPs convert dissolved ozone to hydroxyl radicals, a process which occurs more rapidly as pH is elevated (e.g., varying from a slow reaction at pH 6 and below, to an instantaneous reaction at pH 9 and above). The ability of hydroxyl radicals to inactivate microbes is not well defined, and specific CT values for AOPs have not been developed because (a) the half-life of hydroxyl free radicals is on the order of microseconds and (b) the highest concentration of hydroxyl free radicals that can be developed in aqueous solution is on the order of 10^{-12} Molar. Therefore, the Manufacturers of some AOP systems may choose to conduct microbial seeding or challenge testing to show the level of inactivation that can be achieved for a specific process. Manufacturers of some ozone systems may also choose to conduct microbial inactivation studies for equipment verification.

Labatiuk, Belosevic, and Finch (1994) recommended that ozone disinfection processes should maintain a stable ozone residual for disinfection prior to the addition of hydrogen peroxide for oxidation of other compounds. If water treatment equipment employing an AOP concept provides for detention time in which water can be in contact with dissolved ozone for a significant time before the application of hydrogen peroxide or ultraviolet radiation, evaluation of CT values attained prior to conversion of ozone to hydroxyl radicals may be possible. In this situation, AOP systems could be tested to develop CT information, but the manufacturer's statement of performance regarding disinfection capability would have to be limited to the portion of the treatment process in which a dissolved ozone residual is maintained.

3.0 GENERAL APPROACH

Testing of equipment covered by this ETV plan will be performed by an NSF-qualified Field Testing Organization (FTO) that is selected by the equipment Manufacturer. Water quality and microbiological analytical work to be carried out as part of this ETV plan will be contracted with a state-certified or third party- or EPA-accredited analytical laboratory.

4.0 OVERVIEW OF TASKS

4.1 Initial Operations: Overview

The purpose of these tasks is to provide preliminary information, which will facilitate final test design and data interpretation. Initial Operations Tasks A and B are not mandatory but they are recommended as an aid to successful completion of Verification Testing. Furthermore, if the verification entity conducts a site visit for quality assurance (QA) purposes, the Task B would need to be performed.

4.1.1 Task A: Characterization of Feed Water

The objective of this Initial Operations task is to obtain a chemical and physical characterization of the feed water for those systems using ozone or AOPs for inactivation. The biological quality of the feed water shall be determined for those plants conducting microbiological seeding or challenge testing.

A thorough description of the watershed or aquifer and any pretreatment modules that provide the feed water should also be prepared to aid interpretation of feed water characterization.

4.1.2 Task B: Initial Test Runs

During Initial Operations, the equipment Manufacturer may want to evaluate equipment operation and determine flow rates, hydraulic retention time, contact times (via tracer tests), ozone dosage, number of ozone injection points, pH range, temperature, alkalinity, sequencing or timing of UV light/hydrogen peroxide addition relative to ozonation, or other factors which provide effective treatment of feed water. This is a recommended Initial Operations task.

The equipment Manufacturer may also want to work with the FTO and analytical laboratory to perform blank or preliminary challenges and sampling routines to verify that sampling equipment can perform its required functions including microorganism survivability (if conducting microbiological challenge testing). This is also a recommended Initial Operations Task.

4.2 Verification Operations: Overview

The verification testing objective is to operate the treatment equipment provided by the equipment Manufacturer and to assess its ability to meet stated water quality goals and any other performance characteristics specified by the Manufacturer. Equipment shall be operated for a minimum of one test period to collect data on equipment performance and water quality for purposes of performance verification. The test period(s) selected should represent the worst-case for concentrations of ozone demanding contaminants (e.g., iron, manganese, organics, hydrogen sulfide, pesticides, or turbidity).

4.2.1 Task 1: Verification Testing Runs and Routine Equipment Operation

To characterize the technology in terms of efficiency and reliability, water treatment equipment that includes ozone (or AOPs) shall be operated for Verification Testing purposes with the operational parameters based on the results of the Initial Operations testing (see Task B).

4.2.2 Task 2: Feed Water and Finished Water Quality

During each Verification Testing period, feed water and treated water samples shall be collected and analyzed for those parameters relevant to oxidation performance and microbial inactivation or for those parameters affecting equipment performance, as outlined in Section 10, Table 1.

4.2.3 Task 3: Documentation of Operating Conditions and Treatment Equipment Performance

During each Verification Testing run, operating conditions and performance of water treatment equipment shall be documented. This includes ozone feed gas concentration, gas and liquid pressures, gas and liquid temperatures, gas and liquid flow rates, ozone off-gas concentration, applied and transferred ozone dosage, power usage for the ozone generator, ozone transfer equipment, ozone feed-gas and off-gas monitors (if part of the ozone system) and ozone destruct unit, as well as stability of the electrical power supply (surges, brown-outs, etc.).

If ozone (or an AOP) is used following pretreatment (e.g., coagulation/settling), then a complete description of the pretreatment process shall be provided. For AOP systems, the operating conditions and parameters associated with hydrogen peroxide or UV light equipment must also be documented.

4.2.4 Task 4: Microbial Inactivation

The ability of water treatment ozone equipment to achieve microbial inactivation will be demonstrated by maintaining a level of performance criteria (CT value) for ozone systems. Microbial seeding studies to verify microbial inactivation will be allowed in lieu of the performance criteria (CT value) requirement. To evaluate microbial inactivation by hydroxyl radicals in AOP systems (i.e. after addition of hydrogen peroxide or after use of UV light), microbial seeding studies are required.

4.2.5 Task 5: Data Management

The objective of this task is to establish an effective field protocol for data management at the field operations site and for data transmission between the FTO and NSF for data obtained during the Verification Testing. Prior to the beginning of field testing, the database design must be developed by the FTO and reviewed and approved by NSF. This will ensure that the required data will be collected during the testing, and that it can be effectively transmitted to NSF for review.

4.2.6 Task 6: Quality Assurance/Quality Control (QA/QC)

An important aspect of Verification Testing is the protocol developed for quality assurance and quality control. The objective of this task is to assure accurate measurement of operating and water quality parameters during ozone equipment

Verification Testing. Prior to the beginning of field testing, a QA/QC plan must be developed which addresses all aspects of the testing process. Each water quality parameter and operational parameter must have appropriate QA/QC measures in place and documented. For example, the protocol for ozone measurement using a spectrophotometer should describe how the instrument is calibrated, what adjustments are made, and provide a permanent record of all calibrations and maintenance for that instrument.

5.0 TESTING PERIODS

A minimum of one verification testing period shall be performed. Additional verification testing periods may be necessary to verify the manufacturer's performance objectives, such as in the treatment of surface water where additional testing during each season may assist in verifying an objective. For systems treating solely groundwater or surface waters of consistent quality due to pre-treatment, one verification testing period may be sufficient. If one verification testing period is selected, the feed water should represent the worst-case concentrations of contaminants which can verify the manufacturer's performance objectives. Although one testing period satisfies the minimum requirement of the ETV program, manufacturers are encouraged to use additional testing periods to cover a wider range of water quality conditions.

The required tasks in the Verification Testing Plan (Tasks 1 through 6) are designed to be carried out during each testing period. Each testing period shall provide for at least 200 hours of ozone equipment operation. During this time, the performance and reliability of the equipment shall be documented.

Some systems may operate for less than 24 hours per day. Interruptions in ozone production are allowed but the reason and duration of all interruptions shall be fully described in the Verification Testing report. Any testing conducted at intervals less than 200 hours is considered a test *run*, whereas the entire 200 hours (either continuous or as the sum of individual test runs) of ozone equipment operation is considered the Verification Test *period*. If ozone production is interrupted during a verification test run, that test run shall be considered to have been concluded at the time of interruption of the ozone feed. After restart, all data collected are to be part of a new verification test run.

6.0 DEFINITION OF OPERATIONAL PARAMETERS

Definitions that apply to ozone and AOP processes are given below. Refer to Appendix A of *Ozone in Water Treatment, Application and Engineering*, by the American Water Works Association Research Foundation and Compagnie Générale des Eaux, Lewis Publishers, 1991 for a more detailed description of terms.

6.1 Feed Gas or Ozone Production Concentration (% weight or g/m^3 NTP)

The feed gas or ozone production concentration (Y_1) is the ozone concentration (in gaseous form) being applied to the water being treated. It is expressed in units of g/m^3 normal temperature and pressure (NTP) or as percent by weight. The temperature and pressure values associated with NTP are 0°C and one atmosphere (i.e., 14.696 psi, 760 mm Hg, or 101.325 kPa), respectively.

6.2 Off Gas Concentration (% weight or g/m^3 NTP)

The off gas concentration (Y_2) is the ozone concentration (in gaseous form) of the gas which is being released (i.e., off gas) from the water being treated. This off gas contains ozone, which was not transferred into a dissolved form during treatment. It is expressed in units of g/m^3 NTP or as percent by weight.

6.3 Applied Ozone Dosage (mg/L)

The amount of ozone added to the water being treated is the applied ozone dosage. The equation for calculating the applied ozone dosage is as follows:

$$D = P/(8.34\ L)$$

where:
- D = applied ozone dosage (mg/L)
- P = ozone production (lb/day)
- L = water flow rate (MGD, million U.S. gallons per day)

6.4 Transfer Efficiency (percent)

The transfer efficiency is defined as the percentage of ozone that becomes dissolved into the water being treated. The equation for calculating the transfer efficiency is as follows:

$$TE = [(Y_1 - Y_2)/Y_1]*100$$

where:
- TE = transfer efficiency (percent)
- Y_1 = ozone production concentration (g/m^3 NTP or percent by weight)
- Y_2 = off gas ozone concentration (g/m^3 NTP or percent by weight)

This calculation assumes that the flow of the feed gas is equal to the flow of the off gas. The transfer efficiency calculation can be refined by measuring both gas flow rates or by monitoring the dissolved gas concentration in the liquid phase if the Manufacturer desires.

6.5 Transferred Ozone Dosage (mg/L)

The transferred ozone dosage is the concentration of ozone that becomes dissolved into the water being treated. The equation for calculating the transferred ozone dosage is as follows:

$T = (D * TE)/100$

where: T = transferred ozone dosage (mg/L)
D = applied ozone dosage (mg/L)
TE = transfer efficiency (percent, i.e., 95.0 and not 0.95)

6.6 Dissolved Ozone Concentration (mg/L)

The concentration of ozone in solution is the dissolved ozone concentration. It is measured using an indigo bleaching technique (e.g., HACH AccuVac or *Standard Method* 4500-O_3 B) or by inserting a dissolved ozone probe into the process stream. The procedure for calibration of ozone probes is described in Section 14.4.7. The dissolved ozone concentration is used to calculate CT values.

6.7 CT (mg-minute/L)

The product of the dissolved ozone concentration 'C' in mg/L and the contact time 'T' in minutes is referred to as the CT value. CT is the number produced by multiplying these two values together. Thus, equivalent CT values can be produced by a small C multiplied by a large T or a large C for a small T. For example, if the dissolved ozone concentration after 10 minutes of contact time is 0.5 mg/L, the CT value is 10 * 0.5 = 5 mg-minute/L.

The CT value is used as a surrogate measure of disinfection effectiveness for certain microorganisms by assuming that adequate inactivation has occurred when water is exposed to a given disinfectant concentration for a given contact time. The CT value required for achieving a specific level of disinfection by ozone depends on the temperature and pH of the water being treated.

If an ozone system uses side stream injection for ozone application, none of the sample ports used for collecting samples that will be analyzed for ozone concentration may be located at the ozone side stream. All sample ports used for collecting samples needed for determining CT values shall be located in the main ozone contactor where the bulk flow of water is being disinfected.

The USEPA has outlined a recommended method for calculating CT values for conventional ozone contactors in Appendix O of the *Guidance Manual for the Surface Water Treatment Rule*. Two methods of calculating the total CT of a contactor can be used during Verification Testing: conservative and log integration.

6.7.1 Conservative Method of Determining CT Values

For contactors with multiple sampling ports, the CT value for each sample port (calculated using the measured dissolved ozone concentration and the appropriate contact time represented by the individual sample port) can be summed to calculate the overall CT value for the contactor. The T_{10}/T_{theory} factor (which shall be determined during the hydrodynamic tracer tests described in Chapter 1, Protocol for Equipment Verification

Testing of Microbiological Contaminant Inactivation) is then applied to the summed CT values to account for any short circuiting within the contactor. This method of determining CT value is referred to as the "conservative" approach.

The T_{10} value represents the minimum length of time for which 90 percent of the water will be exposed to the disinfectant within the contactor (as determined using tracer testing) while T_{theory} represents hydraulic detention time of the contactor (calculated by dividing the total volume of the contactor by the water flow rate).

An example using the conservative approach follows: if there are three sample ports, located along the ozone contactor at 2, 4, and 6 minutes of hydraulic detention time, and the dissolved ozone concentrations are 1.0, 0.7, and 0.5 mg/L at each sample port, respectively, the summed CT value for a contactor having a T_{10}/T_{theory} of 0.8 would be calculated as follows:

$$CT = (T_{10}/T_{theory}) * [(C_{port\ 1} * T_{port\ 1}) + (C_{port\ 2} * T_{port\ 2\text{-}port\ 1}) + (C_{port\ 3} * T_{port\ 3\ -\ port\ 2})]$$

$$CT = (0.8) * [(1.0 \text{ mg/L} * 2 \text{ min.}) + (0.7 \text{ mg/L} * 2 \text{ min.}) + (0.5 \text{ mg/L} * 2 \text{ min.})]$$

$$CT = 3.52 \text{ mg-minute/L}$$

6.7.2 Log Integration Method of Determining CT Value

From the equation for the conservative method of determining CT values, it can be concluded that the addition of more sampling points would result in a more accurate determination of the actual disinfection environment in the ozone contactor. Since it may be impractical to add more sampling ports to an ozone contactor, a log integration approach may be used during Verification Testing.

If the rate of ozone decay follows first order reaction kinetics, the ozone residual at any point in the contactor can be calculated (Coffey and Gramith, 1994). By measuring the ozone residual at two points (the upstream location, which may be the ozone application point, and the downstream location) in the contactor where the detention time between those two points is known, the ozone decay rate, k, can be calculated. With a constant decay rate and a known initial ozone residual, the log integration method can be used to calculate the CT value. The equation used to calculate CT values based on the log integration method is as follows:

$$CT = (T_{10}/T_{theory}) * (C_o) * (e^{(kt)}-1)/k$$

where: T_{10}/T_{theory} = Short-circuiting factor determined during tracer tests (< 1.0)
C_o = Initial concentration of dissolved ozone at the upstream sampling point, mg/L
k = Decay rate, 1/minute
t = Contact time at the downstream location, minutes

The decay rate, k, is determined using the following equation:

$k = -[\ln C - \ln C_o]/t$

where: C = Dissolved ozone concentration at downstream location, mg/L

Note that the C_o concentration is the measured dissolved ozone concentration at the upstream sampling location and C_o is not the applied ozone dosage.

The log integration method provides a higher, more accurate CT value than the conservative method. The following example illustrates how to calculate the CT values using the log integration method.

If there are two sample ports, located along the ozone contactor at 0 and 6 minutes of hydraulic detention time, and the dissolved ozone concentrations are 1.4 and 0.5 mg/L at each sample port, respectively, the log integrated CT value for a contactor having a T_{10}/T_{theory} of 0.8 would be calculated as follows:

First, calculate the decay rate, k:

$k = -[\ln C - \ln C_o]/t$

$k = -[\ln (0.5) - \ln (1.4)]/6$ min

$k = -[(-0.693) - (0.336)]/6$

$k = 0.172$/min

Next, calculate the CT value:

$CT = (T_{10}/T_{theory}) * (C_o) * (e^{(kt)} - 1)/k$

$CT = (0.8) * (1.4) * (e^{(0.172 * 6)} - 1)/0.172$

CT = 11.8 mg-minutes/L

This comparison shows that the log integration method can give higher CT values than the conservative method.

7.0 TASK A: CHARACTERIZATION OF FEED WATER

7.1 Introduction

This Initial Operations task is performed to determine if the chemical, biological, and physical characteristics of the feed water are appropriate for the water treatment equipment to be tested.

Initial Operations Tasks A and B are not mandatory but they are recommended as an aid to successful completion of Verification Testing.

7.2 Objectives

The objective of this task is to obtain a complete chemical and physical characterization of the source water, or the feed water after pre-treatment that will be entering the treatment system being tested.

7.3 Work Plan

During this Initial Operations task, the following water quality characteristics of the feed water to the ozone system should be measured and recorded for both ground and surface waters: ozone demand, turbidity, temperature, pH, alkalinity, calcium, total hardness, total sulfides, total organic carbon, dissolved organic carbon, ultraviolet absorbance (at 254 nm), color, bromide, iron, and manganese.

Sufficient information shall be obtained to illustrate the variations expected to occur in these parameters that will be measured during the Verification Testing for a typical annual cycle for the water source. This information will be compiled and shared with NSF so NSF and the FTO can determine the adequacy of the data for use as the basis to make decisions on the testing schedule.

A brief description of the watershed or aquifer source shall be provided, to aid in interpretation of feed water characterization. The watershed description should include a statement of the approximate size of the watershed, a description of the topography (i.e., flat, gently rolling, hilly, mountainous) and a description of the kinds of human activity that take place (i.e., mining, manufacturing, cities or towns, farming, wastewater treatment plants) with special attention to potential sources of pollution that might influence feed water quality. The presence of livestock as well as the existence of other wildlife (e.g., beavers) in the watershed shall be reported. The nature of the water source, such as stream, river, lake or man-made reservoir, should be described as well. Aquifer description should include (if available) the above characterization relative to the recharge zone, a description of the hydrogeology of the water bearing stratum(a), well boring data, and any Microscopic Particulate Analysis data indicating whether the groundwater is under the influence of surface waters. Any information pertaining to the nature of the well and aquifer (e.g., shallow well or vulnerable well) should also be included.

Any pretreatment, including oxidation, coagulation, or pH adjustment, of the water upstream of the ozone equipment shall be completely documented and characterized. Any coagulant or other chemical addition shall be identified and the chemical form and dosage shall be fully described.

7.4 Analytical Schedule

There is no recommended analytical schedule for characterization of the feed water. Any existing water quality data should be reviewed to assess the character of the feed or source water as well as the range of water quality that can be expected during each season. Water quality sampling can be performed if there are data gaps in the existing information.

7.5 Evaluation Criteria

Feed water quality will be evaluated in the context of the Manufacturer's statement of the equipment performance objectives but should not be beyond the range of water quality suitable for treatment for the equipment in question. The device shall be tested using water of the quality for which the equipment was designed.

8.0 TASK B: INITIAL TEST RUNS

8.1 Introduction

During the Initial Operations, a Manufacturer may choose to evaluate equipment operations and determine flow rates, hydraulic residence time, ozone production, CT results, and power supply requirements, or other factors applicable to the technology and related to effective treatment of the feed water. The Manufacturer may also choose to work with the FTO and the analytical laboratory to perform blank or preliminary challenges (if necessary) and sampling routines to verify that sampling equipment can perform the required functions under normal operating conditions. This information may also indicate operating conditions under which the Manufacturer's stated performance objectives are not met, or whether any CT values cannot be achieved. This is a recommended Initial Operations task. An NSF field inspection of equipment operations and sampling and field analysis procedures may be carried out during the initial test runs, and if this occurs, the Initial Operations Task B must be performed.

The "EPA/NSF ETV Protocol For Equipment Verification Testing For Inactivation Of Microbiological Contaminants: Requirements For All Studies" (Chapter 1) under which this test plan is formulated requires hydraulic tracer testing to demonstrate flow conditions and residence times (i.e., T_{10} times) in the ozone equipment. The equipment Manufacturer may want to conduct such tests during these initial runs.

The hydrodynamic tracer testing may be done at the ETV field test site, or at another location, including the manufacturer’s plant. Testing at a location other than the field test site may be advantageous in terms of using dye tracers, sampling and analysis, etc. The tracer testing must be conducted by the FTO, regardless of the site chosen for this testing. Performing hydrodynamic tracer tests at a location other than the ETV field test site is an option only if the treatment equipment has an ozone contact chamber produced by the manufacturer and if this contact chamber is the standard chamber provided with the treatment equipment.

Additional tracer tests are required if flow rates or hydraulics differ from those demonstrated previously (i.e., other Verification Testing). Procedures for developing a tracer test methodology are described in the Protocol.

8.2 Objectives

The objective of these test runs is to bracket the proper operating parameters for treatment of feed water during Verification Testing. The disinfection ability of an ozone system will vary depending on the quality of the feed water being treated and the season. Therefore, conducting initial test runs is strongly recommended.

8.3 Work Plan

Because Initial Operations test runs are not a requirement of this ETV plan, the Manufacturer and FTO can decide the duration of Initial Operations. Enough time should be available to establish optimal operating conditions and to ensure that the system will be able to meet any performance objectives.

8.4 Analytical Schedule

Because these runs are being conducted to define future operating conditions for Verification Testing, a strictly defined schedule for sampling and analysis does not need to be followed. Adhering to the schedule for sampling and analysis to be followed during Verification Testing is recommended, however, so the operator can gain familiarity with the time requirements that will be applicable during Verification Testing. Also during the Initial Operations phase, NSF may conduct an initial on-site inspection of field operations, sampling activities, and on-site analyses. The sampling and analysis schedule to be used during Verification Testing shall be followed during the on-site inspection.

8.5 Evaluation Criteria

The Manufacturer should evaluate the data produced during the Initial Operations to determine if the water treatment equipment performed in a manner, which will meet or exceed the statement of performance objectives. If performance is not as good as claimed in the statement of performance objectives, the Manufacturer may conduct additional Initial Operations or cancel the remainder of the testing program.

9.0 TASK 1: VERIFICATION TESTING RUNS AND ROUTINE EQUIPMENT OPERATION

9.1 Introduction

Water treatment equipment that includes ozone or AOPs shall be operated for verification testing purposes with the operational parameters appropriate for the manufacturer's statement of performance objectives.

9.2 Experimental Objectives

The objective of this task is to operate the ozone or AOP equipment and characterize the effectiveness and reliability of the equipment.

9.3 Work Plan

9.3.1 Verification Testing Runs

The Verification Testing Runs in this task consist of an evaluation of the treatment system, using the most successful treatment parameters defined during Initial Operations. Performance and reliability of the equipment shall be tested during one or more Verification Testing periods consisting of at least 200 hours of ozone production at the test site. If only one testing period is used, the time selected should represent the worst-case for concentrations of ozone-demanding contaminants. During each testing period, Tasks 1 through 6 shall be conducted simultaneously.

Operation to treat a range of feed water quality is recommended for equipment treating surface waters because of the differences in water quality that can occur on a seasonal basis, although pre-treatment modules, when present, may dampen these variations. Factors that can influence microbial inactivation include:

- The presence of ozone-demanding substances that may be present in the form of particulate matter, dissolved organic matter, or dissolved inorganic matter; often occurring in the spring, or during reservoir or lake turn-over events, or also encountered in rivers carrying a high sediment load or in surface waters during periods of high runoff resulting from heavy rains or snow melt. Algae also exert an ozone demand, as do iron, manganese, and cyanide. The presence of ozone-demanding substances will affect the CT value achieved by the system.

- pH: which can vary seasonally, will affect the decay rate of ozone in natural waters, and may also affect the CT values achieved by the system.

- Temperature: the required CT values for *Giardia* and viruses are higher for colder water.

- Other ozone-demanding substances.

9.3.2 Routine Equipment Operation

If the water treatment equipment is being used for production of potable water during the time intervals between verification runs, routine operation of the equipment will occur. In this situation, the operating and water quality data collected and furnished to the Safe Drinking Water Act (SDWA) primacy agency shall be supplied to the NSF-qualified FTO for use in evaluating conditions during verification testing.

For equipment that is being used to treat water for distribution to customers, it is assumed that the State has already issued a permit (if one is necessary) for installation and operation. If verification testing is being conducted to establish the inactivation capabilities of the existing equipment, permission by the State may be required if the system were taken off-line for Verification Testing.

9.4 Schedule

During Verification Testing, water treatment equipment shall be operated for a minimum of 200 hours. The reason and duration of any interruptions in ozone production during Verification Testing shall be fully documented.

9.5 Evaluation Criteria

The goal of this task is to operate the equipment for 200 hours during each Verification Testing period. Data shall be provided to substantiate that 200 hours of operation have been completed.

10.0 TASK 2: FEED WATER AND TREATED WATER QUALITY

10.1 Introduction

Water quality data shall be collected during Verification Testing for the feed water and treated water as shown in Table 1. The Field Test Organization, on behalf of the equipment Manufacturer, shall assure the sampling or measuring of the water quality parameters in Table 1. The FTO may use local personnel to assist in collection of samples or measurement of test parameters, but is responsible for their training to assure proper techniques are used at all times.

10.2 Experimental Objectives

The objective of this task is to identify the presence and concentration of water quality characteristics, which might affect the ability of ozone to inactivate microorganisms. This task also may be conducted to provide data on the effect of ozone use on the formation of disinfection by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs) in the test water.

10.3 Work Plan

The Manufacturer or FTO will be responsible for establishing the testing operating parameters, on the basis of the Initial Operations testing. Many of the water quality parameters described in this task will be measured on-site by the NSF-qualified FTO or by local community personnel properly trained by the FTO. Analysis of the remaining water quality parameters will be performed by a state-certified or third party- or EPA-accredited analytical laboratory. The methods to be used for measurements of water quality parameters in the field are listed in the Analytical Methods section in Table 2. The analytical methods utilized in this study for on-site monitoring of feed water and treated water qualities are described in Task 6, Quality Assurance/Quality Control (QA/QC). Where appropriate, the *Standard Methods* reference numbers for water quality parameters are provided for both the field and laboratory analytical procedures. EPA Methods for analysis of the parameters listed in Table 2 also may be used.

Any disinfectant added upstream of the ozone addition point will affect the ozone demand; therefore, an agreement between NSF, the manufacturer, and the FTO must be made to determine whether or not to allow pre-disinfection prior to ozonation during the Verification Testing Period. If a pre-disinfectant is used, testing shall be conducted to verify that no disinfectant residual exists at the influent of the ozone contactor, or if a disinfectant residual does exist, a quenching solution (e.g., sodium bisulfite or hydrogen peroxide) shall be used. The latter option (quenching) is less desirable because the concentration of the quenching agent will have to be carefully monitored during testing to minimize over-feeding of the quenching agent (which would result in an ozone demand).

10.4 Analytical Schedule

Water quality data shall be collected at the intervals specified in Table 1. Additional sampling and data collection may be performed at the discretion of the Manufacturer. Sample collection protocol shall be defined by the FTO in the PSTP. Algae sampling is not required for systems using groundwater sources.

For water quality samples that will be shipped to a state-certified or third party- or EPA-accredited laboratory for analysis, the samples shall be collected in appropriate containers (containing preservatives as needed) prepared by the laboratory. These samples shall be preserved, stored, shipped, and analyzed in accordance with appropriate procedures and holding times, as specified by the laboratory. Original field sheets and chain-of-custody forms shall accompany all samples shipped to the laboratory. Copies of field sheets and chain-of custody forms for all samples shall be provided to NSF.

10.5 Evaluation Criteria

Evaluation of water quality in this task is related to the manufacturer's statement of performance objectives for plants that employ ozone or AOPs in the treatment process.

11.0 TASK 3: DOCUMENTATION OF OPERATING CONDITIONS AND TREATMENT EQUIPMENT PERFORMANCE

11.1 Introduction

Throughout the Verification Testing period, operating conditions shall be documented. This shall include descriptions of pretreatment chemistry and filtration performance for the system processes, if used, and their operating conditions. The performance of the ozone equipment (including ozone generator(s), air preparation system(s), off-gas destruct unit(s), injection equipment, ozone monitor(s), and contactor(s)) as well as UV light and hydrogen peroxide equipment shall be documented. The total volume of water treated and the total power usage for all equipment associated with the ozone or AOP system shall also be recorded.

11.2 Objectives

The objective of this task is to accurately and fully document the operating conditions during treatment, and the performance of the equipment. This task is intended to collect data that describe operation of the equipment and information that can be used to develop cost estimates for operation of the equipment.

11.3 Work Plan

During Verification Testing, treatment equipment operating parameters for both pretreatment and ozonation shall be monitored and recorded on a routine basis by the NSF-qualified FTO or by local community personnel properly trained by the FTO.

Table 3 outlines some of the operating parameters that shall be monitored throughout Verification Testing. Operating parameters, in addition to those listed in Table 3, may be needed to adequately assess the operating conditions of the ozone or AOP equipment. These additional parameters shall be identified by the Manufacturer and the FTO and agreed upon by the Manufacturer and NSF.

Examples of operational parameters that shall be monitored are:

- water flow rates
- gas flow rates
- water pressures
- gas pressures
- water temperatures
- gas temperatures
- ozone operating voltage
- ozone production power consumption
- air preparation power consumption or other consumables for air preparation
- oxygen feed rate (if applicable) and other pertinent operation information
- performance of oxygen generation or oxygen feed equipment
- ozone electrical frequency, if variable
- amperage of ozone equipment.

On a daily basis, the operator shall note and record whether any visual effects of ozonation are apparent in the treated water or on piping or vessels that convey or hold treated water. This may include surface scum, precipitation of metals, color changes, etc. At the end of the test period, if an ozone contact chamber is provided with the equipment and if it is accessible, the contact chamber shall be inspected for deposits of scum, precipitation of metals, or color changes, and this information shall be noted in the Verification Testing report.

11.4 Schedule

Table 3 presents the schedule and recording data required for ozone and AOP systems. The length of time (hours) of operation (during Verification Testing) shall be recorded for all of the ozone and AOP equipment.

11.5 Evaluation Criteria

Where applicable, the data developed from this task will be compared to statements of performance objectives. If no relevant statement of performance objectives exists, results of operating and performance data will be tabulated for inclusion in the Verification Report.

12.0 TASK 4: DOCUMENTATION OF EQUIPMENT PERFORMANCE: CALCULATION OF CT AND (OPTIONAL) INACTIVATION OF MICROORGANISMS

12.1 Introduction

Inactivation of microorganisms is one of the primary purposes of ozone in drinking water treatment modules. The ability of ozone and AOP equipment to inactivate certain microorganisms can be assessed by determining the CT values that can be attained by the equipment under carefully defined water quality and operating conditions and/or measuring the inactivation of microorganisms by conducting challenge testing.

The ability of ozone to inactivate virus and *Giardia* is well documented and the USEPA, in its guidance manual to the states, has adopted a CT approach for determining inactivation of these microorganisms by disinfection. The USEPA has not yet adopted CT values for *Cryptosporidium*, because researchers are still carrying out studies on this (March 1999).

Microbial seeding studies can also be performed to determine the inactivation ability of the ozone equipment being tested. This will be necessary for AOPs, the performance of which cannot be estimated by using CT calculations. The measurement of inactivation is a comparison of the percent of viable organisms in the feed stream with the percent of viable organisms in the effluent.

12.2 Experimental Objectives

The objective of this task is to determine the CT capabilities of the equipment (based on data from Tasks 2 and 3), and if microbial challenge testing is performed, to determine the logs of inactivation achieved during these tests.

12.3 Work Plan

The manufacturer shall conduct water quality sampling and calculate CT values attained by the equipment. In some instances, microbial challenge testing will be used to determine the level of log inactivation that can be achieved by the ozone or AOP equipment.

12.3.1 CT Criteria

The CT concept of assessing disinfection is described in detail in Section 6.6. The data that are needed to calculate CT values include: dissolved ozone concentration at appropriate monitoring points, pH, temperature, and water flow rate and T_{10} contacting time. The CT values necessary to achieve inactivation of viruses, *Giardia*, and *Cryptosporidium* are different from one another and are described in the next two sections.

12.3.1.1 Required CT for Virus and *Giardia*. The EPA-published CT values associated with inactivation of viruses and *Giardia* cysts are shown in Tables 4 and 5, respectively. If the Manufacturer's statement of performance is presented in terms of logs of inactivation of viruses or *Giardia* cysts, the calculated CT values for an ozone system or for an AOP system that provides for dissolved ozone contact in the water being treated before introduction of hydrogen peroxide or UV radiation must exceed the relevant EPA-published CT values shown in Tables 4 and 5. Because CT values for viruses and *Giardia* cysts are temperature dependent, testing should be scheduled to include the extreme range in water temperatures expected to occur during different seasons of the year. The range in water temperatures being treated shall be determined and agreed upon by the FTO and the Manufacturer during the Initial Test Runs conducted prior to Verification Testing.

If a Manufacturer's statement of performance presents log inactivation values that exceed those shown in Tables 4 and 5, or presents log inactivation values for water quality conditions not included in Tables 4 and 5, microbial challenge or seeding studies shall be required to verify the levels of inactivation achieved by the equipment.

If the pH of the feed water to the ozone or AOP system is less than 6 or greater than 9, microbial challenge studies are required for Verification Testing.

12.3.1.2 CT Calculations for *Cryptosporidium*. The USEPA has not developed CT values for estimating the log inactivation of *Cryptosporidium* by disinfection, and as of March 1999 regulatory requirements for *Cryptosporidium* have not been promulgated. During verification testing, the CT value achieved by the equipment shall be determined, regardless of the level of *Cryptosporidium* inactivation that has occurred. However, if a Manufacturer states that the equipment can achieve a certain level of *Cryptosporidium* inactivation, microbial challenge testing must be performed.

12.3.2 Microbial Challenge Tests

Microbial challenge tests, if undertaken, shall be conducted at full scale with commercially available equipment and not with pilot or prototype equipment. The FTO shall conduct the challenge studies in the field, and the FTO shall submit the resulting samples to a state-certified or third party- or EPA-accredited laboratory. Water produced during challenge testing shall not be distributed to the public. Challenge organisms to be tested will be selected by the equipment Manufacturer. Microbial challenge tests shall be performed three times per Verification Test period.

As a QA/QC measure, one additional process control microbial seeding test shall be performed while the ozone equipment is not operating. This seeding test shall be performed after the three microbial challenge tests have been completed, and the system has been flushed with at least three volumes of water (with ozone equipment in use) to ensure that all seeded organisms have exited the system.

If the Manufacturer's Statement of Performance Objectives is based on microbial inactivation, the FTO shall identify the microbiological contaminant inactivation capabilities in the Statement of Performance Objectives provided in the PSTP. In the Statement of Performance Objectives, the Manufacturer shall identify the specific microbiological contaminants to be monitored during equipment testing and the specific operational conditions under which inactivation testing shall be performed. The Statement of Performance Objectives prepared by the FTO on behalf of the Manufacturer shall also indicate the range of water quality under which the equipment can be challenged while successfully treating the feed water. Examples of satisfactory Statements of Performance Objectives based on microbial inactivation were provided below.

> <u>*For Microbial Inactivation*</u>*:*
> *"This system is capable of achieving 3-log_{10} inactivation of Giardia lamblia at a generation system output of 80% for a feed water flow of 100 gpm for a feed water with pH of 8.5 or less, turbidity of 20 NTU or less, organic carbon concentrations between 2.0 and 4.0 mg/L and alkalinity less than 150 mg/L as $CaCO_3$."*
>
> <u>*Microbial Inactivation (Comparative)*</u>*:*
> *"This system is capable of achieving 3-log_{10} inactivation of Giardia lamblia at CTs 20% lower than EPA's published chlorine CTs. This level of Giardia lamblia inactivation will be achieved by the equipment at a generation system output of 80% for a feed water flow of 100 gpm for a feed water with pH of 8.5 or less, turbidity of 20 NTU or less, organic carbon concentrations between 2.0 and 4.0 mg/L and alkalinity less than 150 mg/L as $CaCO_3$."*

12.3.2.1 Organisms Employed for Challenge Experiments. Microorganisms that may be used for inactivation studies are listed below. These species represent microorganisms of particular interest and concern to the drinking water industry, and represent a range of resistance to inactivation methods. The specific batches of microorganisms used in inactivation testing must be shown to be initially viable by the laboratory involved in the analytical aspects of the testing.

Protozoan cysts and oocysts: *Giardia muris, Giardia lamblia, Cryptosporidium parvum*
Bacteria: *Bacillus subtilis, Pseudomonas* spp., *Clostridium perfringens,*
Virus: MS2 bacteriophage (surrogate)

12.3.2.2 Spiking Protocols. The total number of organisms required to provide steady-state microbiological populations will depend on the overall volume of the disinfection contactor, the flow rate through the contactor, the detection limits of the analytical methods, the number of surviving microorganisms at the end of the test, and the duration of the experiments. For viruses, a steady-state final concentration large enough to show 4-log inactivation in the effluent is necessary. For all organisms, the laboratory (ies) supplying the organisms and performing the viability studies shall be experienced in challenge testing and be able to predict initial dosages required to overcome any inherent experimental losses. Microbial challenges shall be conducted either by batch seeding or by feed stream injection.

12.3.2.3 Batch Seeding. A batch feed tank with sufficient volume to provide the required test volume shall be used. The discharge from this tank shall be located so that 100% of the contents can be delivered to the system. The tank shall be filled with feed water that shall be dechlorinated, if necessary. The feed water shall be stirred during dechlorination. Verification of dechlorination shall be performed prior to the introduction of the seed organisms. The feed tank shall be continuously stirred during seeding and throughout the testing period. Prior to microbial seeding of the tank, agitation of the bulk seed container received from the supplier (by vortexing or sonication) shall be employed to assure organisms are not clumped together. A secondary source of feed water (dechlorinated, if necessary) sufficient to provide 3 retention time equivalents (as determined by tracer tests or as defined by system functions) shall be available to add to the tank when the initial contents have been consumed. The purpose of this feed water will be to continue flushing seeded organisms through the ozone contactor to the effluent sample ports.

12.3.2.4 In-line Injection. The microorganism feed suspension will be plumbed into the test unit with a check-valve equipped injection port followed by a mixing chamber. A one liter carboy equipped with a bottom dispensing port will feed this injection port by means of a metering pump (diaphragm or peristaltic or equivalent) via siliconized or Teflon tubing. The pump shall be capable of fluid injection into the pressurized system feed line for the duration of the test, at a measurable and verifiable rate such that the one-liter carboy is depleted coincident with the end of the test.

The carboy with the spiked suspension will contain a magnetic stir bar, will be filled with one liter of system water (dechlorinated if necessary), and will be placed on a stirplate. The stock suspension of microorganisms shall be agitated by methods such as vortexing or sonication prior to being added to the carboy. After the appropriate flow rate has been established through the ozone contactor, the contactor is operating properly, and sample collection systems are readied, the injection pump can be started. During the course of the test run, monitoring of the flow rate through the ozone contactor and the spike injection rate shall be performed at regular intervals. Adjustments to these flow rates will be made to maintain test conditions.

12.3.3 Test Operation and Sample Collection

12.3.3.1 Test Stream Sampling. Sample ports shall be provided for the feed water stream (spiked with concentrations of microbiological contaminants) and the ozone-treated water stream at the contactor effluent. The FTO shall specify the specific ways in which sample collection is performed according to the organisms that will be used for the proposed microbiological inactivation experiments. Examples of potential sample collection methods for bacterial, viral and protozoan organisms are provided below. The methods described, or any other peer-reviewed method may be used for verification testing. The FTO shall propose in the PSTP the specific methods that are to be used for viability assessment of the selected microorganisms (See Section 12.3.5 below).

For bacterial and/or viral seeding experiments, methods for organism spiking and sample collection shall be consistent with a selected peer-reviewed method. The frequency and number of samples collected for each sampling point will be determined by the length of the test run and shall be specified by the FTO in the PSTP. The volume of each ozone-treated water sample from the disinfection contactor effluent will depend on the concentrations of test organisms spiked, and the requirements of the analytical laboratory.

For protozoan spiking experiments, EPA Method 1622 or any other method that has been evaluated through the peer-reviewed process (e.g., Nieminski and Ongerth, 1995) may be followed for sample collection from the spiked water streams. The sample collection system shall be plumbed to allow installation of housings and filters for capture of sufficient flow for microbiological analysis. The FTO shall provide an indication of the recovery efficiency achievable under the sample collection method selected for use during protozoa seeding studies. The specific capture filter recovery system shall be fully described in the PSTP by the FTO. In addition, the PSTP shall include a plan of study for verification testing with a minimum of three standard recovery efficiency tests from the microbiological laboratory.

The sample tap(s) shall be sanitized with 95% ethanol one minute prior to initiating any bacteria or virus sample collection. Taps shall be flowing at the appropriate sample rate for at least one minute prior to sample collection.

12.3.3.2 Chlorine Residual Analysis. The chlorine concentration of the dilution water used for preparing microorganism spiking solutions shall be measured to ensure that no chlorine residual is present.

12.3.3.3 Post-Test Sample Handling. At completion of the test run, the FTO shall disconnect the capture filter holders from the sample taps. Filters shall then be handled and prepared for delivery to the analytical laboratory as directed by that laboratory. The FTO shall then take steps to contain and/or sanitize any organisms remaining in the system. Depending on the unit (design and materials), sanitization may be done using steam or hot water (80°C for 10 minutes). The QA/QC plan should address how this sanitization procedure is to be done to ensure inactivation of live organisms and subsequent removal of inactivated organisms from the unit. The plan should also address biosafety concerns for both humans and the environment.

12.3.4 Experimental Quality Control

Two QA/QC samples shall be included in the microbial challenge tests: 1) process control; and, 2) trip control. The requirements associated with these QA/QC samples are discussed in Task 6, Section 14.5.

12.3.5 Viability Analysis

Methods for assessing the viability of the selected bacteria and viruses shall be specified by a laboratory that is certified, accredited or approved by the state, a third party organization (i.e., NSF) or the USEPA for the appropriate microbial analyses. Selected viability methods shall be specified by the FTO in the PSTP.

Methods for assessing the viability of cysts and oocysts are non-standard but may be used in verifying objectives that an ozone treatment system inactivates protozoan cysts and oocysts if the method has undergone peer review. A summary and comparison of viability methods is presented in research completed by the following researchers: Korich et al. (1993), Nieminski and Ongerth (1995), Slifko et al. (1997) and others (see Section 16.0 References in this Test Plan). Interim, non-standard methods for assessing the viability of cyst and oocyst (e.g., excystation, DAPI/PI) may be used for verification of inactivation after exposure to disinfectants. However, any interim organism viability method is subject to review by experts of cyst and oocyst viability and subsequent method change. Any non-standard method for assessing cyst and oocyst viability shall be correlated to animal infectivity. Microbial viability analyses are further discussed in Section 4.4 of the "Protocol For Equipment Verification Testing of Microbiological Contaminant Inactivation."

Prior to microbial challenge testing, an adequate method of determining viability should be selected to provide meaningful results for the study. For example, the experimental set-up for viability analyses should be able to adequately show the range of log inactivation capabilities of the ozone system being tested.

12.4 Analytical Schedule

For CT value determinations, during the 200 hours of ozone production for Verification Testing, the dissolved ozone residual shall be measured at specified sampling locations and at regular intervals. These intervals shall be three times per day (3/d) if ozone production is continuous over the 200 hour testing period or three times per staffed shift (3/shift) if ozone production is to be periodically interrupted or terminated during Verification Testing such that the periods of ozone production are less than 24 hours. For example, if a system operates for only 8 hours each day, Verification Testing will be conducted over a total of 25 days. Each day, dissolved ozone measurements shall be collected at three different times. The pH, temperature, and water flow rate also need to be measured concurrently with the dissolved ozone concentration so the CT values can be calculated accurately.

Microbial challenge testing shall be performed three times during the Verification Test period. The operating conditions shall be the same for each of the three required challenge tests. These challenge tests shall be conducted during the 200 hours of Verification Testing. A recommended schedule for microbial testing would be to begin the challenge testing at 50, 100, and 150 hours of continuous operation. If additional time is needed beyond the 200 hours for Verification Testing, the schedule of testing for all water quality parameters and operational conditions of Tasks 1, 2, and 3 shall be continued until the microbial challenge tests are completed.

12.5 Evaluation Criteria

The CT values measured in this task will be compared to the Manufacturer's statement of performance for the ozone or AOP equipment. These field-measured CT values will be compared to the EPA-published CT values for the level of inactivation of virus and *Giardia* (Tables 4 and 5) achieved by the ozone or AOP system. If microbial challenge testing is performed, the measured log inactivations of microorganisms will be compared to the ozone CT/inactivation relationships established by the USEPA.

The total CT values for the ozone or AOP system will be calculated for each individual sampling time (i.e., three sampling events per day or per shift), therefore each Verification Test period will produce a minimum of 25 individual CT values. The minimum, maximum, and average CT value for each Verification Test shall also be reported.

13.0 TASK 5: DATA MANAGEMENT

13.1 Introduction

The data management system used in the Verification Testing program shall involve the use of computer spreadsheet software and manual recording of the operational parameters for the water treatment equipment on a daily basis.

13.2 Experimental Objectives

The objectives of this task are: 1) to establish a viable structure for the recording and transmission of field testing data so the FTO will provide sufficient and reliable operational data for verification purposes, and 2) to provide the information needed for a statistical analysis of the data, as described in "EPA/NSF ETV Protocol For Equipment Verification Testing For Inactivation Of Microbiological Contaminants: Requirements For All Studies."

13.3 Work Plan

The following protocol has been developed for data handling and data verification by the FTO. Where possible, a Supervisory Control and Data Acquisition (SCADA) system should be used for automatic entry of testing data into computer databases. Specific parcels of computer databases for operational and water quality parameters should then be downloaded by manual importation into Excel (or similar spreadsheet software) as a comma delimited file. These specific database parcels will be identified based upon discrete time spans and monitoring parameters. In spreadsheet form the data will be manipulated into a convenient framework to allow analysis of water treatment equipment operation. Backup of the computer databases to diskette should be performed on a monthly basis at a minimum. When SCADA systems are not available, direct instrument feed to data loggers and laptop computers shall be used when appropriate.

For parameters for which electronic data acquisition is not possible, field testing operators will record data and calculations by hand in laboratory notebooks (daily measurements will be recorded on specially-prepared data log sheets as appropriate). Each notebook must be permanently bound with consecutively numbered pages. Each notebook must indicate the starting and ending dates that apply to entries in the logbook. All pages will have appropriate headings to avoid entry omissions. All logbook entries must be made in black water insoluble ink. All corrections in any notebook shall be made by placing one line through the erroneous information. Products such as "correction fluids" are never to be utilized for making corrections to notebook entries. Operating logs shall include a description of the water treatment equipment (description of test runs, names of visitors, description of any problems or issues, etc.); such descriptions shall be provided in addition to experimental calculations and other items. The original notebooks will be stored on-site; photocopies will be forwarded to the project engineer of the FTO at an agreed upon schedule. This protocol will not only ease referencing the original data, but will also offer protection of the original record of results.

The database for the project will be set up in custom-designed spreadsheets. The spreadsheets will be capable of storing and manipulating each of the monitored water quality and operational parameters from each task, each sampling location, and each sampling time. All data from the laboratory notebooks and data log sheets will be entered into the appropriate spreadsheets. Data entry will be conducted on-site by the designated field testing operators. All recorded calculations will also be checked at this time. Following data entry, the spreadsheet will be printed out and the print-out will be checked against the handwritten data sheet. Any corrections will be noted on the hard-copies and corrected on the screen, and then a corrected version of the spreadsheet will be printed out. Each step of the verification process will by initialed by the field testing operator or engineer performing the entry or verification step.

Each experiment (e.g. each challenge test run or verification run) will be assigned a run number which will then be tied to the data from that experiment through each step of data entry and analysis. As samples are collected and sent to state-certified or third party- or EPA-accredited laboratories, the data will be tracked by use of the same system of run numbers. Data from the outside laboratories will be received and reviewed by the field testing operator. These data will be entered into the data spreadsheets, corrected, and verified in the same manner as the field data.

13.4 Statistical Analysis

Water quality developed from grab samples collected during test runs according to the Analytical Schedule in Task 2 of this Test Plan shall be analyzed for statistical uncertainty. The FTO shall calculate 95% confidence intervals for grab sample data obtained during Verification Testing as described in "Protocol for Equipment Verification Testing of Microbiological Contaminant Inactivation" (Chapter 1). Statistical analysis could be carried out for a large variety of testing conditions.

The statistics developed will be helpful in demonstrating the degree of reliability with which water treatment equipment can attain quality goals. Information on the differences in feed water quality variations for entire test runs versus the quality produced during the optimized portions of the runs would be useful in evaluating appropriate operating procedures.

14.0 TASK 6: QUALITY ASSURANCE/QUALITY CONTROL

14.1 Introduction

Quality assurance and quality control (QA/QC) of the operation of the water treatment equipment and the measured water quality parameters shall be maintained during the Verification Testing program.

14.2 Experimental Objectives

The objective of this task is to maintain strict QA/QC methods and procedures during testing. When specific items of equipment or instruments are used, the objective is to maintain the operation of the equipment or instructions within the ranges specified by the Manufacturer or by *Standard Methods*. Maintenance of strict QA/QC procedures is important in that if a question arises when analyzing or interpreting data collected for a given experiment, it will be possible to verify exact conditions at the time of testing.

14.3 Work Plan

Equipment flow rates and associated signals shall be documented and recorded on a routine basis. Daily routine walk-throughs during testing shall be used to verify that each piece of equipment or instrumentation is operating properly. In-line monitoring equipment, such as flow meters, will be checked to verify that the readout matches with the actual measurement (i.e., flow rate) and that the signal being recorded is correct. The items listed below are in addition to any specified checks outlined in the analytical methods.

14.3.1 Daily QA/QC Verifications

These verifications shall be conducted daily:

- In-line turbidimeter flow rates (verified volumetrically over a specific time period)
- In-line turbidimeter readings checked against a properly calibrated bench-top model

14.3.2 QA/QC Verifications Performed Every Two Weeks

These verifications shall be conducted every two weeks:

- In-line flow meters/rotameters (clean equipment to remove any debris or biological buildup and verify flow volumetrically to avoid erroneous readings).
- In-line turbidimeters, if any, (clean out reservoirs and re-calibrate, if employed)

14.3.3 QA/QC Verifications For Each Testing Period

This verification shall be conducted before testing begins:

- Tubing: Verify that all tubing and connections are in good condition and replace if necessary. For surface water systems, microbial growth could occur between verification test runs, so replacement of tubing prior to each verification test may be necessary.

14.4 On-Site Analytical Methods

The analytical methods utilized in this study for on-site monitoring of raw water and disinfected water quality are described in the following section. Use of either bench-top or in-line field analytical equipment will be acceptable for the verification testing; however, in-line equipment is recommended for ease of operation. Use of in-line equipment is also preferable because it reduces the introduction of error and the variability to analytical results generated by inconsistent sampling techniques.

14.4.1 pH

Analysis for pH will be performed according to *Standard Method* 4500-H^+ or EPA Method 150.1/150.2. A three-point calibration of any pH meter used in this study shall be performed once per day when the instrument is in use. Certified pH buffers in the expected range shall be used. The pH probe shall be stored in the appropriate solution defined in the instrument manual. Transport of carbon dioxide across the air-water interface can confound pH measurement in poorly buffered waters. If this is a problem, measurement of pH in a confined vessel is recommended to minimize the effects of carbon dioxide loss to the atmosphere.

14.4.2 Temperature

Readings for temperature shall be conducted in accordance with *Standard Methods* 2550. Raw water temperatures shall be obtained at least once daily. The thermometer shall have a scale marked for every 0.1°C, as a minimum, and should be calibrated weekly against a precision thermometer certified by the National Institute of Standards and Technology (NIST). (A thermometer having a range of -1°C to +51°C, subdivided in 0.1° increments, would be appropriate for this work.)

14.4.3 True Color

True color shall be measured with a spectrophotometer at 455 nm, using an adaptation of the *Standard Methods* 2120 procedure. Samples shall be collected in clean plastic or glass bottles and analyzed as soon after collection as possible. If samples cannot be analyzed immediately they shall be stored at 4^oC for up to 24 hours, and then warmed to room temperature before analysis. The filtration system described in *Standard Methods* 2120 C shall be used, and results should be expressed in terms of PtCo color units.

14.4.4 Dissolved Oxygen

Analysis for dissolved oxygen shall be performed according to *Standard Method* 4500-O using an iodometric method or the membrane electrode method. The techniques described for sample collection must be followed very carefully to avoid causing changes in dissolved oxygen during the sampling event. Sampling for dissolved oxygen does not need to be coordinated with sampling for other water quality parameters, so dissolved oxygen samples should be taken at times when immediate analysis is going to be possible. This will eliminate problems that may be associated with holding samples for a period of time before the determination is made.

If the sampling probe is not mounted such that the probe is continuously exposed to the process stream, then care must be taken when measuring the dissolved oxygen concentration. For best results, collect the dissolved oxygen sample with minimal agitation and measure the dissolved oxygen concentration immediately. If possible, measure the dissolved oxygen under a continuous stream of sample by placing the tip of the probe in the sample container, allowing the sample to overflow the container while the probe reaches equilibrium (usually less than 5 minutes).

14.4.5 Total Sulfides

Total sulfide samples should also be collected with minimal agitation and analyzed immediately after sample collection. If possible, the sample container should be filled using a piece of flexible Tygon tubing attached to the sampling port. The end of the tubing should be placed at the bottom of the sampling container, and the container filled to overflowing before removing the tubing and tightly capping the container.

14.4.6 Turbidity Analysis (Optional)

Turbidity analyses shall be performed according to *Standard Methods* 2130 or EPA Method 180.1 with either a bench-top or in-line turbidimeter. In-line turbidimeters shall be used for measurement of turbidity in the filtrate waters, and either an in-line or bench-top turbidimeter may be used for measurement of the feedwater

During each verification testing period, the bench-top and in-line turbidimeters will be left on continuously. Once each turbidity measurement is complete, the unit will be switched back to its lowest setting. All glassware used for turbidity measurements will be cleaned and handled using lint-free tissues to prevent scratching. Sample vials will be stored inverted to prevent deposits from forming on the bottom surface of the cell.

The Field Testing Organization shall be required to document any problems experienced with the monitoring turbidity instruments, and shall also be required to document any subsequent modifications or enhancements made to monitoring instruments.

14.4.6.1 Bench-top Turbidimeters. Grab samples shall be analyzed using a bench-top turbidimeter. Readings from this instrument will serve as reference measurements throughout the study. The bench-top turbidimeter shall be calibrated within the expected range of sample measurements at the beginning of equipment operation and on a weekly basis using primary turbidity standards of 0.1, 0.5, and 3.0 NTU. Secondary turbidity standards shall be obtained and checked against the primary standards. Secondary standards shall be used on a daily basis to verify calibration of the turbidimeter and to recalibrate when more than one turbidity range is used.

The method for collecting grab samples will consist of running a slow, steady stream from the sample tap, triple-rinsing a dedicated sample beaker in this stream, allowing the sample to flow down the side of the beaker to minimize bubble entrainment, double-rinsing the sample vial with the sample, carefully pouring from the beaker down the side of the sample vial, wiping the sample vial clean, inserting the sample vial into the turbidimeter, and recording the measured turbidity.

For the case of cold water samples that cause the vial to fog preventing accurate readings, the vial must be allowed to warm up by partial submersion into a warm water bath for approximately 30 seconds.

14.4.6.2 In-line Turbidimeters. In-line turbidimeters are required for filtered water monitoring during verification testing and must be calibrated and maintained as specified in the manufacturer's operation and maintenance manual. It will be necessary to verify the in-line readings using a bench-top turbidimeter at least daily; although the mechanism of analysis is not identical between the two instruments the readings should be comparable. Should these readings suggest inaccurate readings then all in-line turbidimeters should be recalibrated. In addition to calibration, periodic cleaning of the lens should be conducted, using lint-free paper, to prevent any particle or microbiological build-up that could produce inaccurate readings. Periodic verification of the sample flow rate should also be performed using a volumetric measurement. Instrument bulbs should be replaced on an as-needed basis. It should also be verified that the LED readout matches the data recorded on the data acquisition system, if the latter is employed.

14.4.7 Dissolved Ozone

The dissolved ozone concentration can be measured using an indigo bleaching technique, such as *Standard Method* 4500-O_3 B or the HACH Indigo AccuVac method. When sampling for dissolved ozone, it is important to minimize sample agitation and transfer from one container to another. One good sampling technique is to collect the sample directly from the sample tap. If HACH AccuVac vials are used, the tip of the AccuVac can be placed directly into the tap opening where the water is flowing. Apply pressure and snap the tip while it is inside the sample tap opening. The vacuum in the AccuVac vial will draw the water sample into the AccuVac. Once the AccuVac is filled, remove the AccuVac from the sample tap and analyze according the HACH instructions. If necessary, a short piece (i.e., less than 2 feet) of Tygon tubing can be attached to the sample tap for dissolved ozone sampling. If HACH AccuVac vials are not used, use of tubing attached to the sample port for sample collection is recommended to minimize sample agitation and mixing. This tubing should be Tygon and should be no longer than 2 feet in length.

Another method for measuring dissolved ozone is a dissolved ozone probe. These probes can be placed in the process stream to provide continuous measurements of ozone residuals. Check the probe tip daily to ensure that the membrane has been installed properly and that there are no air bubbles underneath the membrane. Also, check that the pressure and flow rate within the contactor are within the appropriate range for the probe being used. The performance of the probe shall be verified on a daily basis by measuring the dissolved ozone concentration with one of the indigo bleaching methods to ensure that the probe is functioning properly.

A third method for measuring dissolved ozone concentrations is an on-line analyzer which uses UV spectrophotometry to measure the gas-phase concentration of ozone which has been stripped from a liquid sample. These analyzers then correlate the gas-phase ozone concentration to the dissolved ozone concentration. These analyzers are calibrated at the factory.

14.4.8 Gas Phase Ozone

Gas phase ozone concentrations can be measured using either UV absorbance ozone monitors or a wet-chemistry test. Ozone monitors are calibrated at the factory and provide a continuous measure of the ozone concentration in gas phase. The wet-chemistry test method of measuring the ozone concentration of a gas stream involves bubbling ozone through a potassium iodide solution, acidification with sulfuric acid, and titration with sodium thiosulfate. This method is described in detail in Rakness *et al*. (1996). During each Verification Test, a wet-chemistry measurement of the ozone feed gas shall be conducted to independently check that the ozone monitor is functioning properly. If ozone monitors are not available, wet-chemistry tests shall be performed three times per day or three times per shift to measure the ozone concentration in the feed gas and off gas.

14.4.9 Hydrogen Peroxide

The concentration of hydrogen peroxide can be measured using one of two spectrophotometric methods: 1) cobalt-bicarbonate and 2) peroxidase. The cobalt-bicarbonate method, described in Masschelein *et al.* (1977), can be used to measure up to 2 mg/L hydrogen peroxide at 260 nm, whereas the peroxidase method, described in Bader *et al*. (1988), can be used to measure up to 1.7 mg/L hydrogen peroxide at 551 nm.

At low pH, ozone and peroxide can be in solution at the same time, because the reaction rate is slow. The presence of ozone interferes with any hydrogen peroxide analysis; therefore, to measure the amount of hydrogen peroxide in the AOP system, ozone production shall be temporarily terminated while hydrogen peroxide samples are being collected and analyzed.

To ensure the proper feed rate of hydrogen peroxide to the AOP system, use a stopwatch to measure the time required to collect a specified volume of hydrogen peroxide stock solution from the feed system. This requires that the hydrogen peroxide feed line to the contactor be temporarily disconnected so that the pumping rate of the stock hydrogen peroxide solution can be measured. Typically, a graduated cylinder is used to collect the pumped hydrogen peroxide sample and the size of the graduated cylinder is such that the length of collection time exceeds 10 seconds.

The strength of the peroxide feed solution can also be determined from the peroxide supplier's shipping information, as long as the peroxide being used for testing has not been: 1) diluted by the user; 2) exposed to contamination (which would affect its strength); 3) stored for longer than one year; or, 4) stored at temperatures greater than 77 °F.

14.5 Chemical and Biological Samples Shipped Off-Site for Analyses

The analytical methods that shall be used during testing for chemical and biological samples that are shipped off-site for analyses are described in this section.

14.5.1 Organic Samples

Samples for analysis of total organic carbon (TOC), dissolved organic carbon (DOC), and UV_{254} absorbance shall be collected in glass bottles supplied by the state-certified or third party- or EPA-accredited laboratory and shipped at 4°C to the analytical laboratory. These samples shall be preserved, held and shipped in accordance with *Standard Method* 5010 B. Storage time before analysis shall be minimized, according to *Standard Methods*.

Assimilable organic carbon (AOC) samples shall be collected in sampling containers supplied by the state-certified or third party- or EPA-accredited laboratory. Sample collection, preservation, and storage requirements are outlined in *Standard Methods* 9060A and 9060B.

14.5.2 Microbial Parameters: Viruses, Bacteria, Protozoa, and Algae

Samples for analysis of any microbial parameter shall be collected in bottles supplied by the analytical laboratory. Microbial samples shall be refrigerated at approximately 2 to 8°C immediately upon collection. Such samples shall be shipped in a cooler and maintained at a temperature of approximately 2 to 8°C during shipment. Samples shall be processed for analysis by a state-certified or third party- or EPA-accredited laboratory within 24 hours of collection. The laboratory shall keep the samples at approximately 2 to 8°C until initiation of processing. TC densities shall be reported as most probable number per 100 ml (MPN/100 mL) and HPC densities shall be reported as colony forming units per mL (cfu/mL).

Methods for assessing the viability of the selected bacteria and viruses shall be specified by the laboratory(ies) performing the analysis and shall be specified in the PSTP. The FTO may select a laboratory that is certified, accredited or approved by the state, a third party organization (i.e., NSF) or the USEPA for analysis of microbial contaminants in water samples.

Methods for assessing the viability of cysts and oocysts are non-standard but may be used in verifying objectives that an ozone system inactivates protozoan cysts and oocysts if the method has undergone peer review. A summary and comparison of viability methods is presented in research completed by the following researchers: Korich et al. (1993), Nieminski and Ongerth (1995), and Slifko et al. (1997). Any non-standard method for assessing cyst and oocyst viability shall be correlated to animal infectivity.

Algae samples shall be preserved with Lugol's solution after collection, stored and shipped in a cooler at a temperature of approximately 2 to 8°C, and held at that temperature range until counted.

14.5.3 Inorganic Samples

Inorganic chemical samples, including alkalinity, shall be collected and preserved in accordance with *Standard Method* 3010B, paying particular attention to the sources of contamination as outlined in *Standard Methods* 3010C. The samples shall be refrigerated at approximately 4°C immediately upon collection, shipped in a cooler, and maintained at a temperature of approximately 4°C during shipment. Samples shall be processed for analysis by a state-certified or third party- or EPA-accredited laboratory within 24 hours of collection. The laboratory shall keep the samples at approximately 4°C until initiation of analysis.

14.5.4 Bromate

Samples for the analysis of bromate samples shall be collected in sampling containers supplied by the state-certified or third party- or EPA-accredited laboratory. Sample collection and storage requirements are outlined in EPA Method 300.1 or shall be provided by the laboratory conducting the analysis.

14.6 Microbial Challenge Testing

The quality control requirement for microbiological testing was specified in Task 4, Section 12.3.4.

14.6.1 Process Control

A second round of testing shall be carried out using procedures described in Section 12.3, Task 4, but without operating the ozone equipment. The purpose of this testing is to evaluate any cumulative effects produced by the equipment, the spiking and sampling procedures, and the sample handling procedures on organism viability. This testing shall not occur until sanitizing agents and inactivated target organisms, whose presence could affect subsequent tests of the unit (*Giardia* and *Cryptosporidium*), have been eliminated from the contactor. The process control samples should show minimal inactivation of the target organism(s) relative to the trip control sample. Significant inactivation of the organisms in the process control sample indicates that some aspect of the process other than ozone disinfection contributes to inactivation of the test organism(s). Repeat testing is required when this is shown to occur.

14.6.2 Trip Control

For tests utilizing spike challenges, a replicate or subsample of the spiking suspension shall accompany the actual spiking suspension from the analytical laboratory. This replicate sample shall undergo all of the processes used on the actual suspension including dose preparation pre-enumeration, shipping, preparation for spiking, and return to the laboratory for enumeration and viability baseline assessment. The trip control samples should show minimal inactivation of the target organism(s). Significant inactivation of the trip control sample indicates that some step in handling the suspension contributed to inactivation of the test organism(s). The seeding tests must be repeated when significant inactivation of the trip control sample is observed.

15.0 OPERATION AND MAINTENANCE

The following are recommendations for criteria for Operation and Maintenance (O&M) Manuals for drinking water treatment equipment employing ozone treatment.

15.1 Maintenance

The Manufacturer shall provide readily understood information on the recommended or required maintenance schedule for each piece of operating equipment including, but not limited to, the following, where applicable:

- ozone generator (dielectric replacement)
- ozone diffusers or injection port, control valves
- ozone destruct unit (catalyst replacement)
- gas phase ozone monitors (for feed gas and off gas)
- dissolved ozone monitoring equipment
- cooling water equipment
- air preparation unit or oxygen feed system for ozone generation
- gas and liquid rotameters

- UV lamps and other relevant equipment
- peroxide feed equipment
- other equipment such as pumps and valves

The Manufacturer shall also provide readily understood information on the recommended or required maintenance for non-mechanical or non-electrical equipment, including but not limited to, the following, where applicable:

- piping
- contactor chamber

15.2 Operation

The Manufacturer shall provide readily understood recommendations for procedures related to proper operation of all equipment. Among the operating aspects that should be addressed in the O&M manual are:

Ozone Generator
- air preparation or oxygen feed requirements (moisture content, filtration requirements, flow rate)
- cooling water requirements (flow)
- range of variable voltage for adjusting ozone output
- proper sequence of operation for start-up and shut-down
- proper sequence of operation for initial start-up or for re-start after maintenance

Ozone Monitors (Gas Phase)
- temperature and pressure compensation
- zeroing and calibration procedures
- proper sequence of operation for start-up and shut-down

Ozone Destruct Units
- heater and/or blower requirements
- catalyst requirements
- proper sequence of operation for start-up and shut-down

Air Preparation or Oxygen Feed Systems
- desiccant requirements and replacement procedures
- filters (maintenance and replacement schedule)
- proper sequence of operation for start-up and shut-down
- supplemental gas (air or nitrogen) flow rate, pressure, and temperature.

Cooling Water System
- maintenance of proper temperature
- monitoring cooling water flow
- pump maintenance

- proper sequence of operation for start-up and shut-down
- maintenance of recirculation equipment, if cooling water is recirculated

Ozone Contactor Systems
- maintenance schedule and procedures
- replacement procedures

UV lamps
- hours of operation (verification procedures)
- UV irradiance (calibration and verification procedures)
- maintenance schedule and procedures
- replacement procedures
- proper sequence of operation for start-up and shut-down

Hydrogen Peroxide Feed System
- procedures for variable speed adjustments to pump
- information about proper tubing type and size
- anticipated schedule for tubing replacement
- storage information (i.e., safety, container type, container material, temperature, length of storage time) for stock hydrogen peroxide solutions
- proper sequence of operation for start-up and shut-down

Control Valves
- open/close indication
- sequence of operations

The Manufacturer shall provide a troubleshooting guide; a simple checklist of what to do for a variety of problems, including but not limited to:
- no flow to unit
- sudden change in flow to unit
- no electric power
- automatic operation (if provided) not functioning
- valve stuck or will not operate

16.0 REFERENCES

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Table 1. Water Quality Sampling and Measurement Schedule

Parameter	Sampling Location	Mandatory (M) or Optional (O)	Frequency*	
			Surface Water Systems	Ground Water Systems
Temperature (°C)	Feed Water Treated Water	M	3/d or 3/shift	3/d or 3/shift
Dissolved Ozone Residual (mg/L)	Treated Water†	M	3/d or 3/shift	3/d or 3/shift
pH	Feed Water	M	3/d or 3/shift	3/d or 3/shift
Total Alkalinity (mg/L as $CaCO_3$)	Feed Water	O	1/d	1/d
Total Organic Carbon (mg/L)	Feed Water	O	1/d	1/50 hours of ozone production
Dissolved Organic Carbon (mg/L)	Feed Water	O	1/d	1/50 hours of ozone production
UV absorbance at 254 nm (1/m)	Feed Water Treated Water	O	1/d	1/50 hours of ozone production
Color (Pt-Co)	Feed Water Treated Water	O	1/d	1/50 hours of ozone production
Turbidity (NTU)	Feed Water Treated Water	O	3/d or 3/shift	3/d or 3/shift
Bromide (mg/L)	Feed Water Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production
Bromate (μg/L)	Feed Water Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production

Table 1. Water Quality Sampling and Measurement Schedule, continued

Parameter	Sampling Location	Mandatory (M) or Optional (O)	Frequency*	
			Surface Water Systems	Ground Water Systems
Bacteria and Viruses	Feed Water Treated Water	M**	A minimum of three triplicate samples per Verification Testing period.	A minimum of three triplicate samples per Verification Testing period.
Protozoa	Feed Water Treated Water	M**	A minimum of three samples per Verification Testing period.	A minimum of three samples per Verification Testing period.
AOC (ug acetate/L)	Treated Water	M	1 per 200 hours	1 per 200 hours
Quenching Solution (mg/L) (e.g., hydrogen peroxide)	Feed Water	M	1/d	1/d
Hydrogen Peroxide (mg/L)	Stock Solution Treated Water	M††	1 per 50 hours 1 per Verification test period	1 per 50 hours 1 per Verification test period.
Total THMs (µg/L) (chloroform, bromoform, bromodichloromethane, dibromochloromethane)	Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production
HAAs (µg/L) (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, dibromoacetic acid)	Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production

Table 1. Water Quality Sampling and Measurement Schedule, continued

Parameter	Sampling Location	Mandatory (M) or Optional (O)	Frequency*	
			Surface Water Systems	Ground Water Systems
Iron (µg/L)	Feed Water	O	1/50 hours of ozone production	1/50 hours of ozone production
Total Manganese (µg/L)	Feed Water Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production
Dissolved Manganese (µg/L) (Manganese concentration passing through 0.2 µm filter)	Feed Water Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production
Total Sulfides	Feed Water	O	1/d	1/d
Dissolved Oxygen	Feed Water Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production
Algal enumeration and speciation	Feed Water	O	1 per Verification Test Period	Not Required
Calcium (mg/L as $CaCO_3$)	Feed Water	O	1/50 hours of ozone production	1/50 hours of ozone production
Total Hardness (mg/L as $CaCO_3$)	Feed Water	O	1/50 hours of ozone production	1/50 hours of ozone production

* 3/d or 3/shift means that the water quality parameter shall be measured either 3 times per day if ozone production is continuous over the 200 hours of Verification Testing, or 3 times per staffed shift if ozone production is periodically terminated or interrupted, and the length of time of ozone production is less than 24 hours. 1/50 hours of ozone production means that the water quality parameter shall be measured once per each 50 hours of ozone production, regardless of interruptions in ozone production.

† The dissolved ozone concentration should be measured at sampling ports within the ozone contactor or immediately at the outlet of the ozone contactor. Multiple sampling ports may need to be sampled to calculate CT values.

** Mandatory if microbial challenge testing is being conducted. If CT calculations are used, these methods are not required.

†† The peroxide concentration of the stock solution shall be checked at the prescribed frequency. The peroxide concentration within the contactor shall be checked once during or immediately prior to the verification testing period, while the ozone equipment is not operating. Peroxide monitoring within the contactor will require that samples be withdrawn at appropriate sampling ports at the end or outlet of the contactor.

Table 2. Analytical Methods

Parameter	Facility	*Standard Methods*[1] number or Other Method Reference	EPA Method[2]
Temperature	On-Site	2550 B	
pH	On-Site	4500-H^+ B	150.1 / 150.2
Total alkalinity	Lab	2320 B	
Total Hardness	Lab	2340 C	
Total organic carbon	Lab	5310 C	
Turbidity	On-Site	2130 B / Method 2	180.1
Dissolved Ozone Residual	On-Site	4500 O_3 B; HACH Indigo Blue Method*	
Iron	Lab	3111 D / 3113 B / 3120 B	200.7 / 200.8 / 200.9
Manganese	Lab	3111 D / 3113 B / 3120 B	200.7 / 200.8 / 200.9
UV_{254} absorbance	Lab	5910 B	
Calcium Hardness	Lab	3500-Ca D	
Dissolved Manganese (manganese passing through 0.2 µm filter)	Lab	3500-Mn	200.0 / 243.2 / 243.3
Bromide	Lab	4500-Br^-	300.0
Total THMs	Lab	6232B	502.2, 524.2, 551
Haloacetic Acids (HAAs)	Lab	6251 B	552.1
Dissolved Organic Carbon	Lab	5310 C	
Color (Pt-Co)	Lab	2120 C	110.2
Total Sulfides	Lab or On-Site	4500-S^{2-} D, E	
Dissolved Oxygen	Lab or On-Site	4500-O	
AOC	Lab	9217	
Bromate	Lab		300.1
Hydrogen Peroxide (mg/L)	Lab or On-site	HACH Method HYP-1 or Masschelein, W., *et al*., (1977) or Bader *et al*. (1988)	
Algal enumeration and speciation	Lab	Part 10000, Biological Examination†	

* Dissolved ozone residual measurements can also be from a properly calibrated and installed dissolved ozone monitor.

† *Standard Methods* does not contain a method for enumeration and speciation of algae. It does, however, contain methods for laboratory techniques, which may need to be performed for proper enumeration and speciation of the algae. Only an experienced and qualified laboratory analyst shall conduct algal enumeration and speciation.

Table 3. Equipment Operating Data

Operational Parameter		Frequency
Water Flow (gpm)	Feed Water	3/d or 3/shift
	Side Stream (if applicable)	3/d or 3/shift
	Cooling Water	3/d or 3/shift
Water Pressure (psig)	Inlet to Ozone System	3/d or 3/shift
	Outlet of Ozone System	3/d or 3/shift
	Side Stream (if applicable)	3/d or 3/shift
	Cooling Water	3/d or 3/shift
Water Temperature (°C)	Inlet to Ozone System	3/d or 3/shift
	Outlet to Ozone System	3/d or 3/shift
	Side Stream (if applicable)	3/d or 3/shift
Gas Phase Ozone Concentration (% wt)	Feed Gas	3/d or 3/shift
	Off Gas	3/d or 3/shift
Power Usage (kw/hr)	Ozone Generator	3/d or 3/shift
	Air Preparation System or Oxygen System	3/d or 3/shift
	Gas Phase Ozone Feed and Off Gas Monitors	3/d or 3/shift
	Cooling Water System	3/d or 3/shift
	Destruct Units	3/d or 3/shift
	Other pumps or motors	3/d or 3/shift
Ozone Feed Gas Temperature (°C)		3/d or 3/shift
Ozone Feed Gas Pressure (psig)		3/d or 3/shift
Ozone Feed Gas Flow (scfm)		3/d or 3/shift
Atmospheric Pressure (psia)		1/d or 1/shift
Dew Point (if using air feed system)		1/d or 1/shift
Ozone Production (lb/d)		1/d or 1/shift
If applicable: Purity of oxygen supply (%) Supplemental nitrogen flow rate (scfm), pressure (psig), and temperature (°C) Supplemental air flow rate (scfm), pressure (psig), and temperature (°C)		 1/d or 1/shift 1/d or 1/shift 1/d or 1/shift
If applicable: Peroxide feed concentration (mg/L) Peroxide feed rate (mL/min) Peroxide to Ozone ratio (by weight)		1/d or 1/shift
If applicable: Operating parameters for UV-light systems (see ETV Testing Plan for Microorganism Contaminant Inactivation by Ultraviolet Based Technology – Chapter 4)		3/d or 3/shift

Table 4. CT Values for Inactivation of *Giardia* Cysts by Ozone at pH 6 to 9

	Temperature (°C)					
Inactivation	0.5	5	10	15	20	25
0.5 log	0.48	0.32	0.23	0.16	0.12	0.08
1.0 log	0.97	0.63	0.48	0.32	0.24	0.16
1.5 logs	1.5	0.95	0.72	0.48	0.36	0.24
2.0 logs	1.9	1.3	0.95	0.63	0.48	0.32
2.5 logs	2.4	1.6	1.2	0.79	0.60	0.40
3.0 logs	2.9	1.9	1.4	0.95	0.72	0.48

Source: Appendix O to the Guidance Manual For Compliance With the Filtration and Disinfection Requirements For Public Water Systems Using Surface Water Sources.

Table 5. CT Values for Inactivation of Viruses by Ozone

	Temperature (°C)					
Inactivation	0.5	5	10	15	20	25
2.0 logs	0.9	0.6	0.5	0.3	0.25	0.15
3.0 logs	1.4	0.9	0.8	0.5	0.4	0.25
4.0 logs	1.8	1.2	1.0	0.6	0.5	0.3

Source: Appendix O to the Guidance Manual For Compliance With the Filtration and Disinfection Requirements For Public Water Systems Using Surface Water Sources.